

NASA TECHNICAL TRANSLATION

1N-27
184705
NASA TT-20204
P-8

ELECTRICALLY CONDUCTING POLYMER-COPPER SULPHIDE
COMPOSITE FILMS, PREPARATION BY TREATMENT OF
POLYMER-COPPER (II) ACETATE COMPOSITES WITH
HYDROGEN SULFIDE

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Kobunshi Ronbunshu, vol. 44, no. 4, pp 327-329,
April 1987

(NASA-TT-20204) ELECTRICALLY CONDUCTING
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(NASA) 8 P

N88-17803

Unclas
CSCL 11B G5/27 0124965

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON D.C. 20546 MARCH 1988

ORIGINAL PAGE IS
OF POOR QUALITY.



Report Documentation Page

1. Report No. NASA TT-20204	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle ELECTRICALLY CONDUCTING POLYMER COPPER SULPHIDE COMPOSITE FILMS. PREPARATION BY TREATMENT OF POLYMER-COPPER (II) ACETATE COMPOSITES WITH HYDROGEN SULFIDE		5. Report Date MARCH 1988	
		6. Performing Organization Code	
7. Author(s) Takakazu Yamamoto, Takahira Kamigaki, Etsuo Kubota		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, DC 20546		11. Contract or Grant No. NASW-4307	
		13. Type of Report and Period Covered translation	
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, DC 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Transl. from JAPANESE into ENGLISH of article from Kobunshi Ronbunshu, vol. 44, no. 4, pp 327-329, April 1987. (Japan)			
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17. Key Words (Suggested by Author(s))		18. Distribution Statement unclassified-unlimited	
19. Security Classif. (of this report) unclassified	20. Security Classif. (of this page) unclassified	21. No. of pages 8	22. Price

ELECTRICALLY CONDUCTING POLYMER-COPPER SULPHIDE COMPOSITE FILMS,
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/327

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(Received October 30, 1986; Accepted February 2, 1987)

Abstract

Polymer-copper sulfide composite films were prepared by treatment of polymer(poly(vinyl chloride), poly(acrylonitrile), copolymer of vinyl chloride and vinyl acetate (90:10), and ABS resin-copper (II) acetate composites with hydrogen sulfide. The films showed electrical conductivity higher than 10^{-11} S cm⁻¹ when they contained more than 20 wt% of copper sulfide. A poly(acrylonitrile)-copper sulfide composite film containing 40-50 wt% of copper sulfide showed electrical conductivity of 10^0 - 10^2 S/cm⁻¹ and had relatively high mechanical strength to be used in practical purposes.

1. Introduction

It is known that electrically conducting composites can be obtained by dissolving an electrically conductive substance in a polymer compound. In the past, metal powder or a carbon type substance has been used for the electrically conductive substance (Reference 1) but recently some electrically conductive composites made of copper sulfide and a polymer compound were introduced (References 2 to 7). The following three preparation methods of the electrically conductive polymer compound containing copper sulfide have been reported. A) The method which makes an electrically conducting copper sulfide layer on the surface of a polymer material by treating the polymer material, where copper compound is absorbed on the surface, with a sulfide compound (References 2, 6 and 7). B) The method which treats a polymer and copper composite with hydrogen sulfide (Reference 3). C) The method in which a polymer compound is dissolved in a solution of copper sulfide colloid;

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then the solvent is removed from the mixture (Reference 4 and 5). It is difficult to obtain an electrically conductive composite with the method which simply mixes copper sulfide and a polymer compound (Reference 4 and 5).

Method B) of the above methods is superior in practical use due to the simple preparation method; however only the application of poly methacrylate-copper complex is reported and the electrical conductivity of the obtained composite is less than about $10^{-1} \text{ S cm}^{-1}$.

The authors' group has developed method C) in the past and reported that the electric conductive composite obtained can be used for preparation of devices such as diodes and etc. as a p-type semi-conductor (Reference 4 and 5). At this time, the authors have expanded the method which has been applied only to poly methacrylate in the past and report the results in which polymer-copper sulfide composites having relatively high electric conductivity of 10^{-1} to 10^0 S cm^{-1} were produced.

2. Experiment method

2.1 Preparation method of composite

After dissolving 160mg of copper (II) acetate (anhydride) in 25 cm^3 of N,N-dimethyl-formamide (DMF), a certain amount of polyvinyl chloride, poly acrylonitrile, copolymer of vinyl chloride and vinyl acetate (90:10) or ABS resin was dissolved in it and the solutions were obtained. The polymer compounds used here were purchased from the Poly-sciences Co.

A part of the uniformly dissolved solution obtained from the above method was put on a glass plate and DMF was removed from the vacuum line; then polymer-copper (II) acetate composite film ($40 \mu\text{m}$ to $100 \mu\text{m}$ thick) in which the copper acetate is uniformly dissolved and has a mechanical strength was obtained. The composite film using poly (N-vinyl-2-pyrrolidone) instead of the above mentioned polymer compounds has less mechanical strength. The composite film from poly vinyl acetate or copolymer of vinyl chloride and acrylonitrile (80:20) has tackiness, so it was not used to make the composite with copper sulfide.

The above polymer-copper (II) acetate composite film having mechanical strength is removed from the glass plate and put into an eggplant shaped flask; then after removing air, dry hydrogen sulfide gas which is produced by a reaction of concentrated phosphoric acid and $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ in the vacuum line was added at room temperature. The pressure of the hydrogen sulfide gas was about 400mmHg and it was about 10 times the moles of copper-acetate in the polymer-copper sulfide composite film.

When dry hydrogen sulfide gas was added, the polymer-copper sulfide composite film /3/ got black immediately. After being left for four days at room temperature so that the reaction could take place, hydrogen sulfide was removed. Then volatile matter such as acetic acid was removed under vacuum conditions and a black polymer-copper sulfide composite film was obtained. In the IR spectrum, absorption of acetic acid was hardly recognized.

2.2 Measurement method

A part of the polymer-copper sulfide composite film was cut off and a piece of film 6mm x 6mm was obtained. Platinum wires were connected to both ends of the piece with conductive resin (Electrodag +502 by Furuuchi Chemicals Co.) and the electrical resistance was measured by the two terminal method. When the electrical resistance is less than about $10^3 \Omega$, the relationships between applied voltage and current were measured with the potentiostat/galvanostat Model HA-301 by Hokuto Electric Co. For electrical resistance more than about $10^5 \Omega$, the Model TR-8651 electrometer by the Taketa Riken Co. was used. The measurement was performed in an environment of argon at room temperature (25 to 30°C).

A powder X-ray diffraction pattern was obtained from the Model PW-1051 by the Phillips Co.

3. Conclusions and considerations

Absorption due to acetic acid or acetic acid radical was not observed in the infrared spectrum of the polymer-copper sulfide composite film. This indicates that copper (II) acetate is almost completely converted to copper sulfide by reaction with hydrogen sulfide. Fig.1 shows the powder X-ray diffraction pattern of the composite obtained in the case of using poly acrylonitrile. The diffraction pattern assigned to copper (II) sulfide appeared clearly and it also indicates the conversion of copper (II) acetate to copper (II) sulfide. The half band width of the diffraction pattern ($2\theta = 17.0^\circ$, Cu-K α line) by the crystal of poly acrylonitrile hardly changed by formation of the composite in Fig.1. For poly acrylonitrile-copper sulfide composite, ν (C $\equiv$ N) absorption did not change by formation of the composite; thus, it seems that the interaction of -CN radical and copper sulfide is not very large.

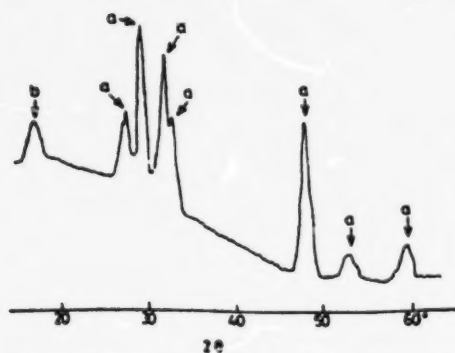


Fig. 1. Powder X-ray (Cu-K α) diffraction pattern of the poly-(acrylonitrile)-copper sulfide composite. Bands with a are assigned to CuS and a band with b is to poly(acrylonitrile).

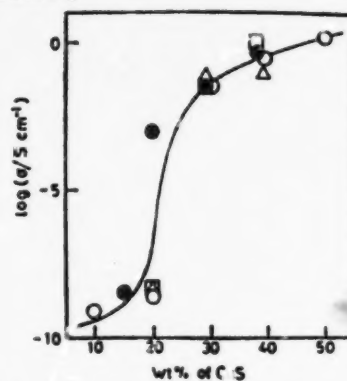


Fig. 2. Dependence of electrical conductivity of polymer-copper sulfide composites on wt% of CuS in the composite at room temperature. (○) for poly(acrylonitrile), (●) for poly(vinyl chloride), (□) for copolymer of vinyl chloride and vinyl acetate (90:10), and (Δ) for ABS resin.

Fig. 2 shows the electrical conductivity of polymer-copper sulfide composite obtained by the above mentioned method. As shown in Fig. 2, the composites are almost insulating materials in the case that the content of copper sulfide is less than 20 to 25 wt% of the composites, but in the case of more than 20 to 25 wt% (about 5% in volume percent), the electrical conductivity rapidly increases to 5 digits. When the content of copper sulfide is more than about 40%, the electric conductivity reaches about 100 S cm^{-1} . This electrical conductivity is higher than the previously reported conductivity of poly methacrylate-copper composite (sulfur content = 0 to about 25 wt%) obtained from the reaction of poly methacrylate-copper complex and hydrogen sulfide. It indicates that copper compound is more converted to copper sulfide in the polymer compound used in this study. From the results of the above infrared spectrum and the powder X-ray diffraction pattern, the weight percent of copper sulfide in the composite in this study was calculated with the assumption that all of the copper acetate was converted to CuS by the reaction with hydrogen sulfide. The copper (II) sulfide obtained by the reaction of copper (II) acetate and $(\text{NH}_4)_2\text{S}$ in DMF was formed in the shape of pellets under 400 kg/cm^2 of pressure after drying. Then the pellet was taken out and the electrical conductivity was measured and the conductivity was 15 S cm^{-1} (Reference 8).

As shown in Fig. 2, the phenomenon in which electrical conductivity of the composite increases when the content of conductivity material increases but the electrical conductivity increases rapidly when the content of the conductivity material reaches $\underline{\quad}$

a certain amount is known for the composites of polymer compound and carbon type material or metal powder (Reference 1). The phenomenon occurs due to the chain reaction of conductivity of the conductive substance formed in the composite (References 1 and 9) and it seems that when the content of the conductive substance reaches a certain amount, the chance of formation of the chain reaction increases rapidly (Reference 1).

The results shown in Fig. 2 can be explained with a similar assumption. The reason the data for 4 types of polymer compound shown in Fig. 2 are almost on the same curve seems to be that the distribution condition of copper sulfide is about the same.

For the 4 types of polymer compound, when the content of copper sulfide increases, all of the composites get brittle. In the case that the content of copper sulfide of ABS resin and copolymer of vinyl chloride and vinyl acetate is less than about 40 wt%, the film has mechanical strength and it can be bent repeatedly, but in the case that the content is more than about 40 wt%, it becomes a brittle film. On the other hand, in the case of using poly acrylonitrile or poly vinyl chloride they still have mechanical strength (tensile strength = 10 kg/cm²) even though the content of copper sulfide reaches 40 wt%, especially in the case of poly acrylonitrile, it has strength at 50 wt% of copper sulfide. As the authors reported previously (References 4 and 5), it seems that polymer-copper sulfide composite can be used for preparation of devices such as diodes. When such application is considered, poly acrylonitrile-copper sulfide composite and poly vinyl chloride-copper sulfide composite which have mechanical strength are especially useful.

By treating the polymer compound-copper acetate composite with (NH₄)₂S solution instead of hydrogen sulfide, a similar black polymer compound-copper sulfide composite mentioned above was obtained and these composites have electrical conductivity. However, the composites produced by this method have a tendency of desorption of the copper sulfide formed in the surface layer.

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